Effect of Chemical Additives on the Alkali-Silica Reaction Product Examined by Transmission Soft X-ray Microscopy

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INTRODUCTION

Worldwide, 104 concrete dams and spillways, massive concrete structures, have been damaged by the alkali-silica reaction (ASR) [1]. Reactive silicates present in some aggregate react with alkalis present in the concrete pore fluid to produce an alkali-silica reaction gel. Overall, two steps comprise the alkali-silica reaction, the dissolution of silica and the formation of a potentially expansive gel product by repolymerization. Swelling of the ASR gel can eventually lead to cracking and overall expansion of the affected structure. As a result of this damage, the structure loses strength, particularly in flexure, stiffness, and impermeability – material properties essential to ensure the integrity and performance of the structure during service. In addition, expansion of the concrete can interfere with clearances required for mechanical elements, such as spillway gates or turbines, in dams. Currently, no practical means exists to arrest ASR once damage is initiated. Reconstruction of affected massive concrete structures, such as dams, is not economically feasible. As a result, structures affected by ASR must be continually monitored so that repair and reinforcement can be performed as needed.

However, research has shown that the introduction of certain chemicals, particularly lithium- and calcium-containing salts and acetone [2], can reduce expansion caused by ASR. Perhaps the most fundamental impedance to the practical use of chemical additives is the lack of knowledge of the mechanisms by which these chemical additives may control expansion. Without understanding the mechanism of control, it is difficult to predict the effectiveness of a chemical additive and to foresee the duration of its control. A more thorough understanding of these mechanisms would aid assessing which chemical are most effective over long periods and which doses are optimal.

OBJECTIVE

The objective was to investigate the mechanisms by which some chemical additives control expansion using transmission soft x-ray microscopy. The reaction of alkali-silicate gel in sodium hydroxide solution in the presence of calcium ions, lithium ions, and acetone was observed using transmission soft x-ray microscopy. These images can be compared to images of the alkali-silicate gel in sodium hydroxide solution, without the chemical additives [3,4], to qualitatively assess the effects of calcium chloride, lithium chloride, and acetone.

EXPERIMENT

Slurries were prepared containing ASR gel and NaOH solutions with $SiO_2/Na_2O=3$, proportions identified [5] to maximize expansion. The ASR gel used in these investigations was obtained from the Furnas Dam located in Minas Gerais, Brazil. The local quartizite aggregate used in the concrete construction was found to be reactive when surface staining, cracking, and the presence of gel were noted in 1995, 32 years after the construction of the dam was completed. To examine the effect of some chemical additives on the ASR gel, the ground gel (~300 sieve) was exposed to four solutions: (a) 0.7M NaOH (control/background), (b) 0.7M NaOH + 0. 1M CaCl₂, (c) 0.7M NaOH + 0.1M LiCl and (d) 0.7M NaOH + 10% (v/v) acetone. The pH of 0.7M NaOH, 0.7M NaOH +

RESULTS

X-ray images show that the reaction of the ASR gel in 0.7M NaOH + 0.1M CaCl $_2$ solution produces lath-like structures (Fig.1). The product morphology is very similar to the spherulitic 'sheaf of wheat' structures produced by the reaction of the alkali-silicate gel in saturated Ca(OH) $_2$ solution [3] and described in the literature as calcium silicate hydrates (C-S-H) or C-S-H precursors [6-8]. It is theorized that the formation of C-S-H or a related compound will decrease the degree of swelling that would otherwise result. The C-S-H-like structure may also contribute strength to the concrete.

X-ray images of alkali-silicate gel in 0.7M NaOH + 0.1M LiCl solution show products of varying morphology (Fig. 2). Small particles ranging from approximately $0.25\mu m$ to $3\mu m$ in size are typical of the sample, and repolymerization is evident in some x-ray images. X-ray images show that the repolymerized gel is apparently of decreased density, as compared to the original particles of ASR gel, and is believed to be the source of expansion. However, the volume of repolymerized produce appears to be less than in 0.7M NaOH without the addition of LiCl.

X-ray images of the alkali-silicate gel in 0.7M NaOH + 10% (v/v) acetone are shown in Figure 3. The images show regions of varying density, similar to the repolymerized alkali-silicate product resulting from the reaction of the ASR gel in 0.7M NaOH. The indication of extensive repolymerization suggests that acetone may not be an effective chemical additive for controlling expansion caused by the alkali-silica reaction.

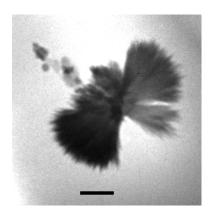


Figure 3. X-ray image of alkalisilicate gel in 0.7M NaOH + 0.1M CaCl₂. The image was taken with a 14.858 s exposure time with a beam current of 201.3 mA at an original magnification of 2400x. scalebar = 1μ m. 71121019

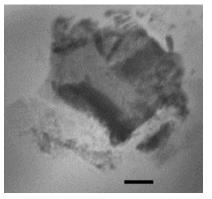


Figure 2. X-ray image of alkalisilicate gel after 1 week in 0.7M NaOH + 0.1M LiCl. The image was taken with a 11.190 s exposure time with a beam current of 267.5 mA at an original magnification of 2400x. scalebar = 1µm. 71015011

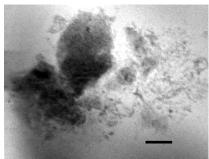


Figure 3. X-ray image of alkalisilicate gel in 0.7M NaOH + 10% acetone by volume. The image was taken with a 8.978 s exposure time with a beam current of 222.3 mA at an original magnification of 2400x. scalebar $= 1 \mu m$. 71024010

CONCLUSIONS

Reaction of the ASR gel in 0.7M NaOH + 0. 1M CaCl₂ solution produced spherulitic structures resembling the distinctive 'sheaf of wheat' morphology which is not believed to be expansive. Images of the reaction of the ASR gel in 0.7M NaOH + 0.1M LiCl solution showed that dissolution of the original gel particles had occurred. However, in the presence of lithium chloride, the repolymerization into an expansive gel was decreased as compared to the reaction of the ASR gel in 0.7M NaOH solution. Images of the reaction of the ASR gel in 0.7M NaOH + 10% (v/v) acetone solution showed alkali-silicate gel particles surrounded by repolymerized gel,

indicating that the use of acetone as a chemical additive may not be as effective as once believed in preventing expansion caused by ASR.

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REFERENCES

- 1. R.G. Charlwood and Z.V. Solymar, Management of AAR-Affected Structures: An International Perspective, 2nd International Conference on Alkali-Aggregate Reaction in Hydroelectric Plants and Dams, Chattanooga, Tennessee, 19, (1995).
- 2. W.J. McCoy and A.G. Caldwell, J. ACI, V47, (1951).
- 3. K.E. Kurtis, P.J.M. Monteiro, J.T. Brown, and W. Meyer-Ilse, "Imaging of ASR gel by Soft X-ray Microscopy", Cement and Concrete Research, V28:411-421 (1988).
- 4. K.E. Kurtis, P.J.M. Monteiro, J.T. Brown, and W. Meyer-Ilse, "In Situ Alkali-Silica Reaction Observed by X-ray Microscopy", Advanced Light Source: Compendium of User Abstracts and Technical Reports 1993-1996, LBNL-39981/UC-411, (1997).
- 5. L.S. Dent Glasser and N. Kataoka The Chemistry of 'Alkali-Aggregate' Reaction, Cement and Concrete Research, V11, 1-9 (1981).
- 6. R.B. Williamson, Constitutional Supersaturation in Portland Cement Solidified by Hydration, *J. Crystal Growth*, V34, 787-794 (1968).
- 7. D. Zampini.; S.P. Shah.; and H.M. Jennings Early Age Microstructure of the Paste-Aggregate Interface and Its Evolution, *J. Materials Res.*, V13, N.7, 1888-98 (1998).
- 8. A.M. Rashed, "The Microstructure of Air-entrained Concrete", UC Berkeley Dissertation, (1989).

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